# Saponification of Wheat Straw-*g*-Polyacrylonitrile

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## Synopsis

Wheat straw-*g*-polyacrylonitrile (PAN), containing 40% PAN, was saponified with sodium hydroxide and isolated under three sets of saponification and work-up conditions. Each reaction mixture was separated into a water-soluble and a water-insoluble fraction, which were individually analyzed for percentages (by weight) of synthetic polymer (saponified PAN), cellulose, hemicellulose, and lignin. Water solubles amounted to 14–24% of the total product and contained 70–74% synthetic polymer, the remainder being hemicellulose and lignin. Although water-insoluble fractions contained 52–54% saponified PAN, their water absorbencies were low (14–17 g $H_2O$/g polymer). Treatment of these fractions with the enzyme cellulase converted 55–62% of the total cellulose to glucose.

## INTRODUCTION

Living plants constitute some of the most complex and best formulated polymeric composites known to man. Although polymeric plant constituents have many useful properties that would be difficult to duplicate synthetically, the number of uses for these materials could be greatly expanded if there were convenient methods for modifying some of the properties of these natural polymers for specific end-use applications. Graft polymerization is one excellent way of achieving this goal, and much has been published on both starch[1] and cellulose[2,3] grafting. Lignocellulosic materials derived from a number of different plant sources have also been used as substrates in these polymerization reactions.[4] Use of whole-plant materials as substrates is less common in the literature, and major contributions in this category have been in the area of wood–plastic composites.[5,6]

Since cereal straw is an abundant source of biomass, we have studied its reactivity in graft polymerization reactions, and a recent paper[7] describes graft polymerization of acrylonitrile onto ground wheat straw. Distribution of polyacrylonitrile (PAN) grafts among the three major straw constituents (cellulose, hemicellulose, and lignin) was also determined. Since the choice of acrylonitrile as monomer for this study was largely due to the importance of saponified polysaccharide-*g*-PAN copolymers as thickening agents and as absorbents for aqueous fluids,[8] we have continued this area of research by examining the saponification of straw-*g*-PAN and the composition and properties of saponification products.

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## EXPERIMENTAL

### Materials

Straw of soft winter wheat (*Triticum aestivum*, variety "Arthur" from central Illinois) was freed of heads, roots, and leaves and ground in a Wiley mill (screen with 2 mm round openings). Ground straw was washed eight times with water at room temperature (100 g straw in 3 L) and was allowed to air–dry to a moisture content of about 8%. Weight loss was 13–14%. Nitrogen analysis of washed straw: 0.2%.

Acrylonitrile (Eastman)* was distilled at atmospheric pressure through a 14 in. Vigreux column.

### Graft Polymerization

Fifteen grams (dry basis) of wheat straw was suspended in 300 mL of 0.001*M* sulfuric acid, and 7.5 mL of a solution of 1.00 g $FeSO_4 \cdot 7H_2O$ in 50 mL of 0.001*M* $H_2SO_4$ was then added. The flask was placed in a 55°C water bath, and a slow stream of nitrogen was passed through the stirred mixture for 1 h. Thirty grams of acrylonitrile were then added, followed after 5 min by a solution of 3.00 g of 31.8% hydrogen peroxide in about 6 mL of water. Polymerization was allowed to proceed for 2 h, and the solid was then separated by filtration, washed with water, and air dried. Homopolymer was removed from the crude graft copolymer by exhaustive extraction with dimethylformamide (DMF), and the graft copolymer was again washed with water and air dried. Kjeldahl nitrogen analysis of the resulting straw-*g*-PAN showed 40% PAN by weight.

### Saponification of Straw-*g*-PAN

**Procedure A.** A mixture of 10.00 g (dry basis) of straw-*g*-PAN and 70 mL of 0.96*N* sodium hydroxide in a loosely stoppered flask was heated in a 100°C oven for 2 h. The reaction mass was diluted with 150 mL of water and was exhaustively dialyzed against distilled water. The dialyzed mixture was filtered through Whatman 52 paper, and the solid was washed three times with water and allowed to air dry. Solid was isolated from the combined filtrate and washings by freeze drying. Moisture contents of both samples were calculated from weight loss after vacuum drying at 100°C over $P_2O_5$. Infrared spectra showed complete nitrile saponification.

**Procedure B.** A mixture of 5.00 g of straw-*g*-PAN and 35 mL of 1.93*N* sodium hydroxide was heated in a 100°C oven for 2 h. The reaction mass was worked-up as in Procedure A; however, centrifugation rather than filtration was used to separate solid due to greater swelling in water. Water-insoluble and water-soluble fractions were both isolated by freeze drying.

**Procedure C.** Straw-*g*-PAN was saponified as in Procedure B, and the reaction mass was then blended with 250 mL of methanol. Solid was separated by filtration, washed three times with methanol, and allowed to air dry to a moisture content of 14%. Air-dried solid was suspended in about

* The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

200 mL of water and was exhaustively dialyzed against distilled water. Insoluble solid was separated and washed with water, and both water-soluble and water-insoluble fractions were isolated by freeze-drying.

## Composition of Saponified Straw-*g*-PAN

**Method for Determining Synthetic Polymer Content.** Saponification of the PAN moiety with sodium hydroxide yields a random copolymer of acrylamide and sodium acrylate. Synthetic polymer content cannot be determined by simply subtracting the weight of straw in the original straw-*g*-PAN from the weight of saponified straw-*g*-PAN, since inorganics and degradation products of straw are lost during dialysis. Synthetic polymer content can be calculated, however, if the amount of polyacrylamide in the whole sample and the ratio of acrylamide to sodium acrylate repeating units in the synthetic portion are known. To determine these quantities, we can assume that the high molecular weight of PAN precludes any loss of saponified PAN through the dialysis membrane. As a result, moles of acrylonitrile repeating unit in our original straw-*g*-PAN would equal moles of acrylamide repeating unit plus moles of sodium acrylate repeating unit in the saponified product:

$$\frac{\text{wt PAN in original straw-}g\text{-PAN}}{53.06} = \frac{\text{wt polyacrylamide in saponified product}}{71.08} + \frac{\text{wt of poly(sodium acrylate) in saponified product}}{94.06}$$

Since weight of polyacrylamide in the saponified product may be determined from Kjeldahl nitrogen analysis, the weight of poly(sodium acrylate) is readily calculated along with the weight percentage of polyacrylamide in the saponified grafts. These polyacrylamide weight percentages were 36.1, 30.1, and 28.4 for Procedures A, B, and C, respectively.

Since the lower polyacrylamide percentage for Procedure C (as compared with B) is probably due to slight product loss resulting from methanol precipitation, a value of 30% polyacrylamide was used for subsequent calcu-

TABLE I
Saponification of Polyacrylonitrile[a]

| Mol NaOH/mol AN[b] | Vol and *N* of NaOH | Heating method | % N | % PAA[c] |
|---|---|---|---|---|
| 0.8 | 15 mL, 1*N* | Oven (3 h) | 7.26 | 36.8 |
| 1.6 | 15 mL, 2*N* | Oven (2 h) | 5.9 | 29.9 |
| 0.8 | 7.5 mL, 1.926*N* | Oven (2 h) | 6.3 | 32.0 |
| 0.8 | 15 mL, 0.9646*N* | Reflux (2 h) | 6.0 | 30.4 |
| 0.8 | 15 mL, 0.9646*N* | Reflux (1¼ h) | 6.2 | 31.5 |

[a] 1.00 g PAN used in each experiment.
[b] AN = acrylonitrile repeating unit.
[c] PAA = polyacrylamide.

lations. Polyacrylamide percentages of this magnitude agree with Kjeldahl nitrogen-determined polyacrylamide contents of a series of polymers that we obtained by saponifying pure PAN (Type A, DuPont) under a variety of different conditions (Table I).

**Isolation of Alkali-Soluble Wheat Straw Lignin and Determination of Extinction Coefficient.** Ground wheat straw (5 g) was heated under reflux for 4 h with 1*N* trifluoroacetic acid to hydrolyze hemicellulose.[9] The water-washed and air-dried residue (2.7 g) was stirred for 5 h at room temperature with 50 mL of 2*N* sodium hydroxide, and the solid separated by filtration and washed with water. To determine whether the extinction coefficient of lignin would change with increasing severity of alkali treatment, another alkali-soluble fraction was obtained by further extracting the wet filter cake with 50 mL of 2*N* sodium hydroxide for 4 h at 100°C. Both alkaline solutions were dialyzed against distilled water and freeze-dried. Solids were converted to the acid form by stirring with 0.1*N* hydrochloric acid, dialyzing, and freeze-drying. Solids were then extracted with 10:90 (vol) methanol–chloroform to separate organic-soluble lignin from residual carbohydrate. Organic solutions were evaporated to dryness, residues were dissolved in 0.1*N* sodium hydroxide, and excess alkali was removed by dialysis. The following alkali-soluble lignins were isolated by freeze-drying: (A) from the room temperature alkali extraction, 58 mg; (B) from the 100°C alkali extraction, 114 mg. Infrared spectra of the two samples were virtually identical, and carbohydrate absorption was absent. A plot of absorbance at the UV maximum of 278 nm vs. concentration of Product B ($7.72 \times 10^{-3}$–$3.86 \times 10^{-2}$ g/L in 0.0127*N* NaOH) gave a straight line with an extinction coefficient ($A_{278}$/g lignin per L) of 22.0. Extinction coefficient of Product A was 24.4.

**Composition of Water-Soluble Fractions.** Lignin was determined from the UV absorbance (278 nm) of solutions prepared in 0.0127*N* NaOH. Calculations were based on experimentally determined extinction coefficients of 22.0 and 24.4, and the two values were averaged. Hemicellulose was determined[9] by refluxing 0.1 g of polymer in 2 mL of 1*N* trifluoracetic acid for 7 h, and then determining xylose concentration in the hydrolyzate by HPLC. A Bio-Rad ion exclusion HPX-87H column was used with water as the mobile phase at a flow rate of 0.6 mL/min. For our calculations, we assumed that wheat straw hemicellulose contains 85% xylan[10–14] and that hydrolysis of xylan to xylose goes to completion. Although Lepoutre et al.[15] reported some water solubility for a saponified cellulose-*g*-PAN prepared from bleached softwood pulp, the absence of significant amounts of cellulose in the water-soluble fraction of saponified straw-*g*-PAN was suggested by totals of 100% (or slightly greater) resulting from addition of weight percentages of synthetic polymer, hemicellulose, and lignin.

**Composition of Water-Insoluble Fractions.** Hemicellulose was determined by trifluoroacetic acid hydrolysis, as described for water-soluble fractions; however, these hydrolyses probably do not go to completion due to the recalcitrant nature of cellulose and lignin. Since we observed previously[9] that wheat straw containing about 29% hemicellulose gave a 23% yield of xylose under these conditions, weight percent hemicellulose in each fraction was obtained by multiplying the xylose yield (from HPLC) by a factor of 29/23. Weight percent cellulose in these fractions was calculated assuming

that all cellulose initially present in straw-*g*-PAN is now present in the insoluble saponified fraction. Wheat straw contains about 33% cellulose,[16] and correcting this value for the amount of noncellulosic material lost through water washing (before graft polymerization) and DMF extraction (after grafting) gives about 41% cellulose in the straw portion of straw-*g*-PAN. Percent lignin in these insoluble fractions was not independently determined but was simply calculated by difference.

### Water Absorbency of Saponified Straw-*g*-PAN

Accurately weighed samples of the three water-insoluble fractions were allowed to swell in excess distilled water, and the weight of swollen polymer was then determined after removal of unabsorbed water by screening.[17] Absorbencies were expressed in g water per g dry polymer.

### Treatment of Saponified Straw-*g*-PAN With Cellulase

Enzyme solution was prepared by dissolving 1.00 g of cellulase (TV Concentrate, Enzyme Products Division, Miles Laboratories) in 100 mL of buffer solution prepared from citric acid (0.05*M*), $Na_2HPO_4$ (0.10*M*), and thymol (0.05%). Eight milliliters of this cellulase solution was added to 0.2 g of saponified straw-*g*-PAN, and the mixture was gently shaken for 22 h at 45°C. The supernatant was separated by filtration, and glucose was determined by HPLC under the same conditions described for xylose.

## RESULTS AND DISCUSSION

Graft polymerization of PAN onto water-washed wheat straw was initiated with $Fe^{+2}$–hydrogen peroxide,[7] and ungrafted PAN was removed by exhaustive extraction with DMF to yield straw-*g*-PAN containing 40% PAN, by weight. Reaction of straw-*g*-PAN with aqueous alkali was carried out at 100°C under three sets of saponification and work-up conditions. Procedure A used 0.8 mol NaOH/mol acrylonitrile in the PAN moiety; this NaOH:acrylonitrile ratio has been successfully used in starch-*g*-PAN saponifications.[18] Additional NaOH was also added to take into account the consumption of alkali by the straw portion of the graft copolymer (e.g., due to saponification of acetyl ester substituents on hemicellulose). In a control experiment, this amounted to 1.4 meq NaOH/g straw. The reaction mass was dialyzed against distilled water to remove excess alkali, and water-soluble and water-insoluble fractions were then separately isolated. Procedure B used twice the concentration of sodium hydroxide used in A, and products were similarly isolated. Procedure C also used twice the amount of NaOH; however, the saponification product was precipitated with methanol and air-dried. The dry product was then dialyzed, and water-soluble and water-insoluble fractions were isolated as in B. This procedure was used to determine whether drying the product prior to water extraction would promote hydrogen bonding and crosslinking, and thus reduce the amount of water extractables.

Water-soluble and water-insoluble fractions obtained by the three procedures were accurately weighed, and weight percentages of synthetic polymer, cellulose, hemicellulose, and lignin in each fraction were determined

by methods described in detail in the Experimental section. Results are presented in Table II. Procedure A was the mildest of the three conditions and gave a significantly lower percentage of water-soluble polymer (14% vs. 22–24% of the total product). Also, grafted branches in the fractions from A had a higher polyacrylamide: poly(sodium acrylate) ratio (see Experimental section). Precipitating the final product with methanol and drying it prior to water extraction (Procedure C) did not greatly reduce water solubles. Water-soluble fractions contain significant percentages of hemicellulose and lignin, while grafted cellulose remains largely in the water insolubles. Percent lignin in water-soluble fractions decreases with increased severity of saponification and is lowest for the methanol-precipitated product, presumably due to removal of organic-soluble lignin fragments. Since total weight of isolated product in each saponification was less than expected, higher than theoretical percentages of synthetic polymer in the various fractions in Table II can be explained by loss through the dialysis membrane of low molecular weight straw components, e.g., inorganic salts and NaOH-induced degradation products of polysaccharide and lignin. Straw-*g*-PAN containing 40% PAN would yield a saponified product containing about 52% synthetic polymer, if there were no loss of straw on saponification.

Although this work was carried out for the primary purpose of investigating the distribution of components in saponified straw-*g*-PAN, we also examined some properties of the three water-insoluble fractions in Table II.

TABLE II
Composition of Saponified Straw-*g*-Polyacrylonitrile

| | Saponification and work-up procedure[a] | | |
|---|---|---|---|
| | A | B | C |
| Water-soluble fraction | | | |
| Weight (g) | 1.56[b] | 1.37[c] | 1.21[c] |
| % N (Kjeldahl) | 5.1 | 4.2 | 4.4 |
| % of Total product | 14.0 | 24.5 | 22.2 |
| Composition (%) | | | |
| Synthetic polymer | 72 | 70 | 74 |
| Cellulose | — | — | — |
| Hemicellulose | 16 | 19 | 19 |
| Lignin | 16 | 12 | 7 |
| Water-insoluble fraction | | | |
| Weight (g) | 9.59[b] | 4.22[c] | 4.23[c] |
| % N (Kjeldahl) | 3.8 | 3.1 | 3.1 |
| % of Total product | 86.0 | 75.5 | 77.8 |
| Composition (%) | | | |
| Synthetic polymer | 54 | 52 | 52 |
| Cellulose | 26 | 29 | 29 |
| Hemicellulose | 12 | 9 | 9 |
| Lignin[d] | 8 | 10 | 10 |

[a] Procedures A, B, and C are given in the Experimental section.
[b] From 10.00 g of straw-*g*-PAN.
[c] From 5.00 g of straw-*g*-PAN.
[d] Calculated by difference.

In particular, we were interested in (1) water absorbency and (2) ease of enzyme hydrolysis of the cellulose component. Water absorbencies of products from Procedures A, B, and C were 14, 17, and 17 g distilled water/g dry polymer, respectively. These values are lower by over a factor of 10 than absorbencies found for saponified starch-*g*-PAN,[17,18] and they are also lower by roughly a factor of 2 than reported values for saponified cellulose-*g*-PAN.[15] Use of whole straw as a substrate for grafting, therefore, offers little advantage in the preparation of water absorbents. Although reasons for this lower absorbency are not known, the hydrophobic and recalcitrant nature of the lignin component is, no doubt, a contributing factor.

Although water absorbency is low relative to starch- and cellulose-based absorbents, saponified straw-*g*-PAN swells sufficiently in water to permit a significant percentage of the cellulose component to be converted to glucose by the enzyme cellulase. Conversion of cellulose to glucose was 55% for the water-insoluble fraction from procedure A, while comparable fractions from procedures B and C gave conversions of about 62%. Cunningham et al.[16] report a cellulose conversion of only about half this magnitude for wheat straw having no chemical modification or pretreatment.

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